LAS in the Environment: Facts and Figures

Ignacio López
CEPSA QUÍMICA S.A
São Paulo, June 2010

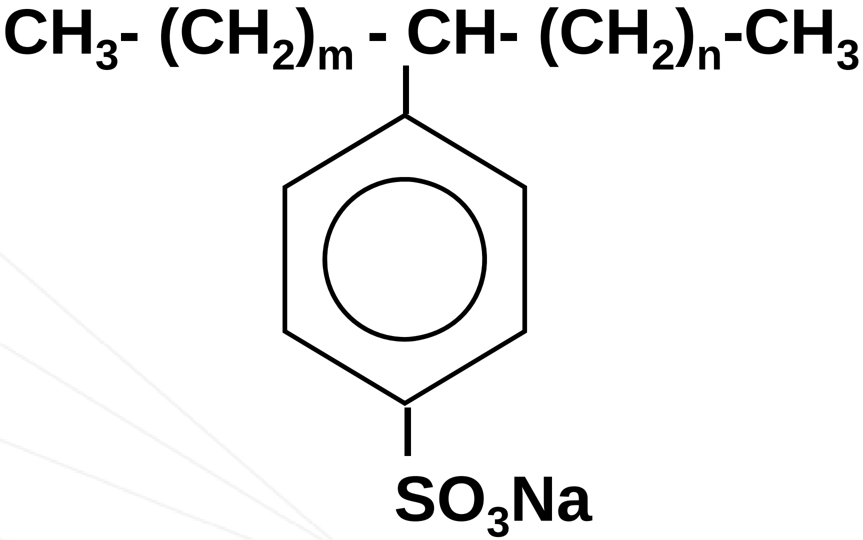
Content

- Background information
  - Product Description
  - Physicochemical Properties
  - Production & Technology
  - Consumption
  - Final Uses
  - Typical Detergent Formulation
- LAS properties
  - Biodegradability in freshwater
  - Anaerobic Biodegradation
  - Aquatic Toxicity
  - Bioconcentration
  - Endocrine Disruptor
  - Conclusions
- Environmental & Human Safety
  - Fate of LAS in the Environment
  - Hazard & Risk. Concepts.
  - Ecotoxicity
  - Risk Assessment
  - Human Safety
  - Life Cycle Inventory (LCI)
  - Conclusions
- Occurrence of foam in the Tiete River
  - Background
  - Results
  - Conclusions

Background

The molecule

CAS Number : 68411-30-3
EINECS Number : 270 - 115 - 0



.m+ n = 7-10
.Linear Alkyl chain
.Benzene ring randomly distributed in all positional isomers except 1-phenyl.
.Sulfonate group in *para* position
.Average Molecular Weight = 342

- LAS is, after soap, the most used surfactant word wide
- LAS was first commercialized in the early 60's as a replacement of the poorly biodegradable DDBS (Dodecyl benzene sulfonate - Branched alkylbenzene sulfonate). This was a voluntary and responsible action, taken by the chemical industry

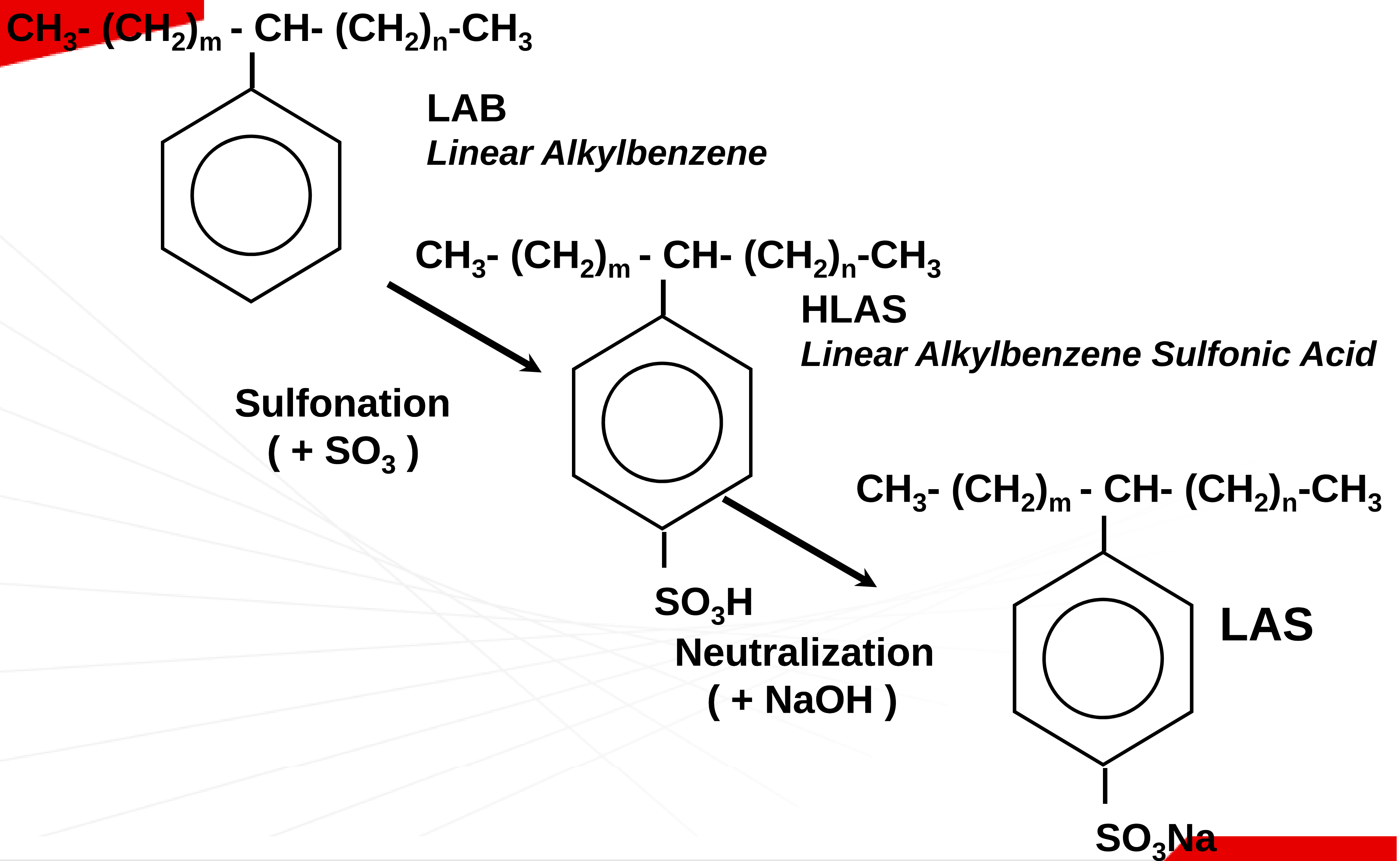
Anionics: The Hydrophilic Moiety has a negative charge

Physicochemical Characteristics

Melting Point	276.8 °C
Boiling “	637.4 “
Specific Gravity	1.06 g/cm^3
Vapor Pressure @ 25°C	1.28 x 10^{-14}
Log P_{ow} (calculated)	2.0152
Solubility (as Na salt)	250 g/l
“ (as Ca salt)	ca. 4 mg/l

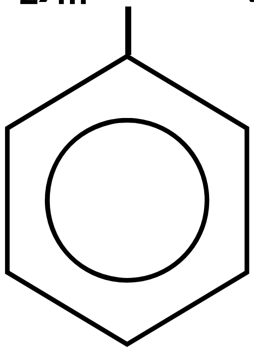
(Data referred to NaLAS ,97wt% active matter conc.)

The Chemistry



The Chemistry

CH_3- $(CH_2)_m$ - CH- $(CH_2)_n$-CH_3



LAB
Linear Alkylbenzene

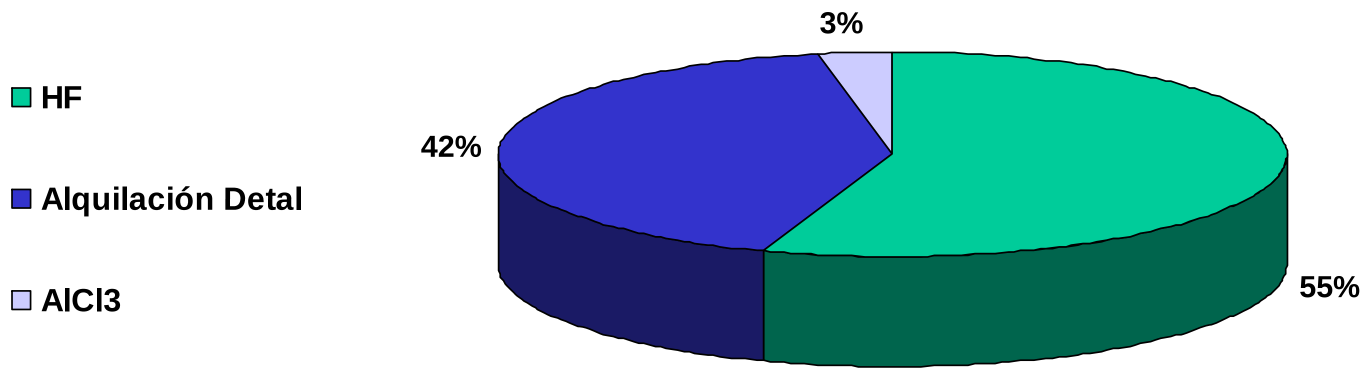
Alkylation **of Benzene with n-olefins or Alkylhalides**

- ***$AlCl_3$***
- ***HF***
- ***Fixed Bed (Detal)***

Berna J.L.et.al. Proceedings AOCS Congress,Montreux,1994
Pujado P. et.al. Tenside Surf.Det. 1986 , 23
Cavalli L.et.al. CESIO Congress,London 1992
Cavalli L.et.al.,Tenside Surf.Det. 1999,36,254

Breakdown by Alkylation's Technology

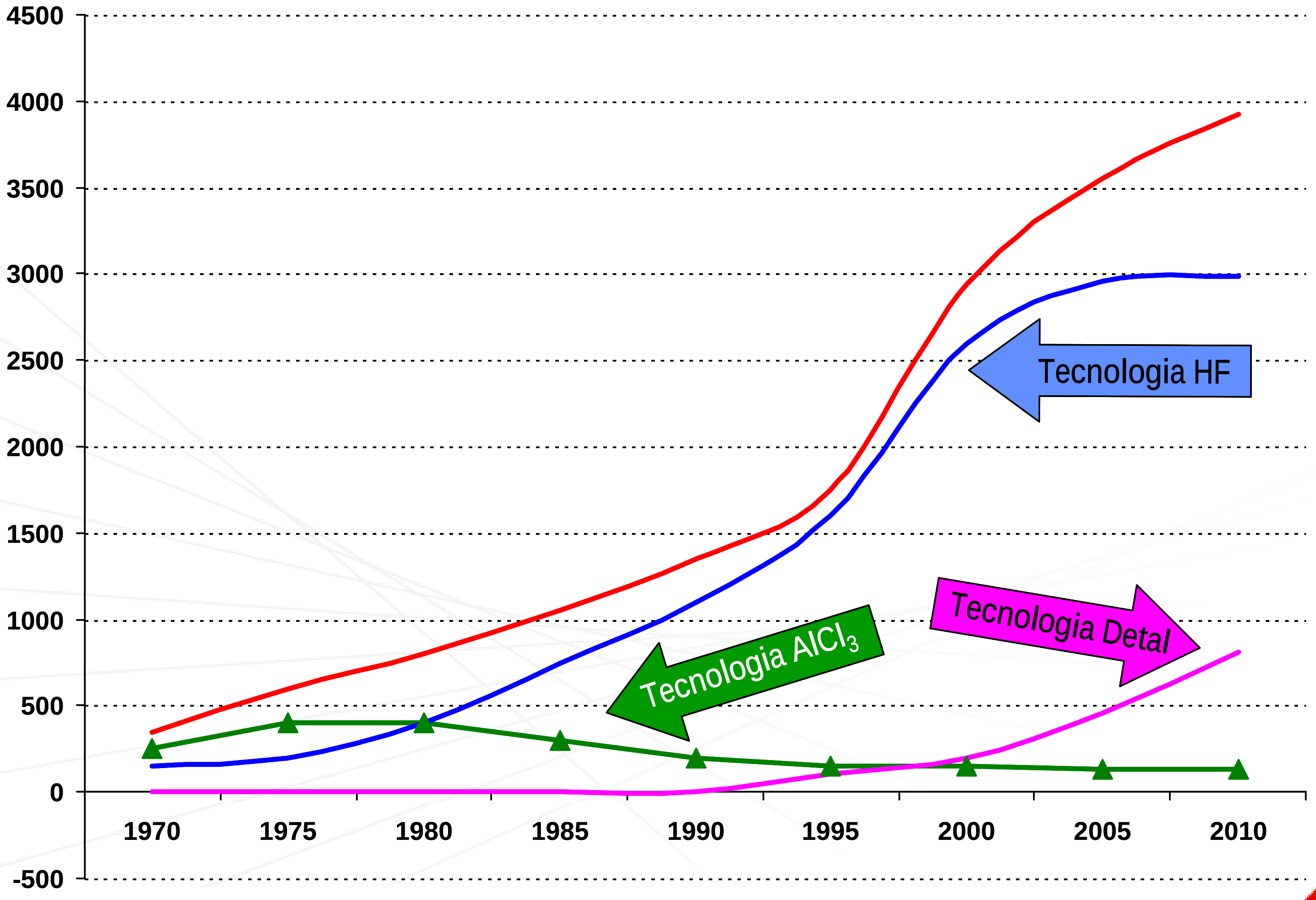
World Production 2006 - 2,9 MM Tm/año



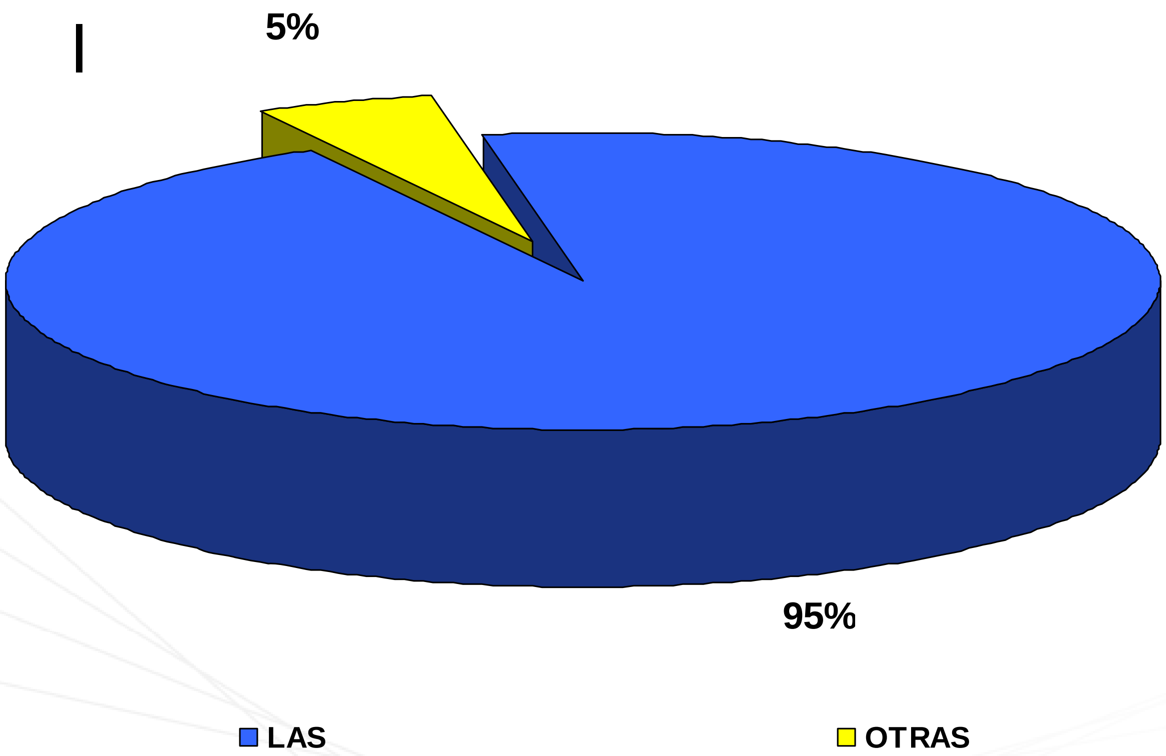
PROCESO	CATALIZADOR	MAT. PRIMA	ETAPAS	PRODUCTO
ALQUILACIÓN CON $AlCl_3$	AlCl3	N-PARAFINAS	• CLORACIÓN • ALQUILACIÓN CON BENCENO	ALTO 2-FENILO (25-30) ALTAS TETRALINAS (5-10)
ALQUILACIÓN HF	HF	N-OLEFINAS INTERNAS	• ALQUILACIÓN CON BENCENO	BAJO 2-FENILO (17) BAJAS TETRALINAS
DETAL	SiO2/Al2O3 F	N-OLEFINAS INTERNAS	• ALQUILACIÓN CON BENCENO	ALTO 2-FENILO (25-30) BAJAS TETRALINAS (<0.5)

Breakdown by Alkylation's Technology

LINEAL ALQUIL BENCENO - PROCESOS DE PRODUCCION



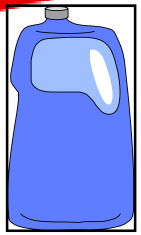
LAB uses

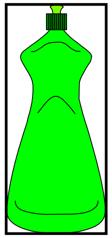


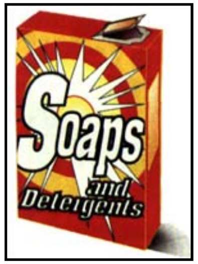
95% of LAB production is transformed into LAS through a sulfonation process. LAS in turn, is almost exclusively used as surfactant ingredient in detergents.

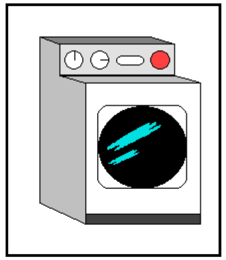
CEPSA

LAS (average) Content in Typical Detergent Formulations





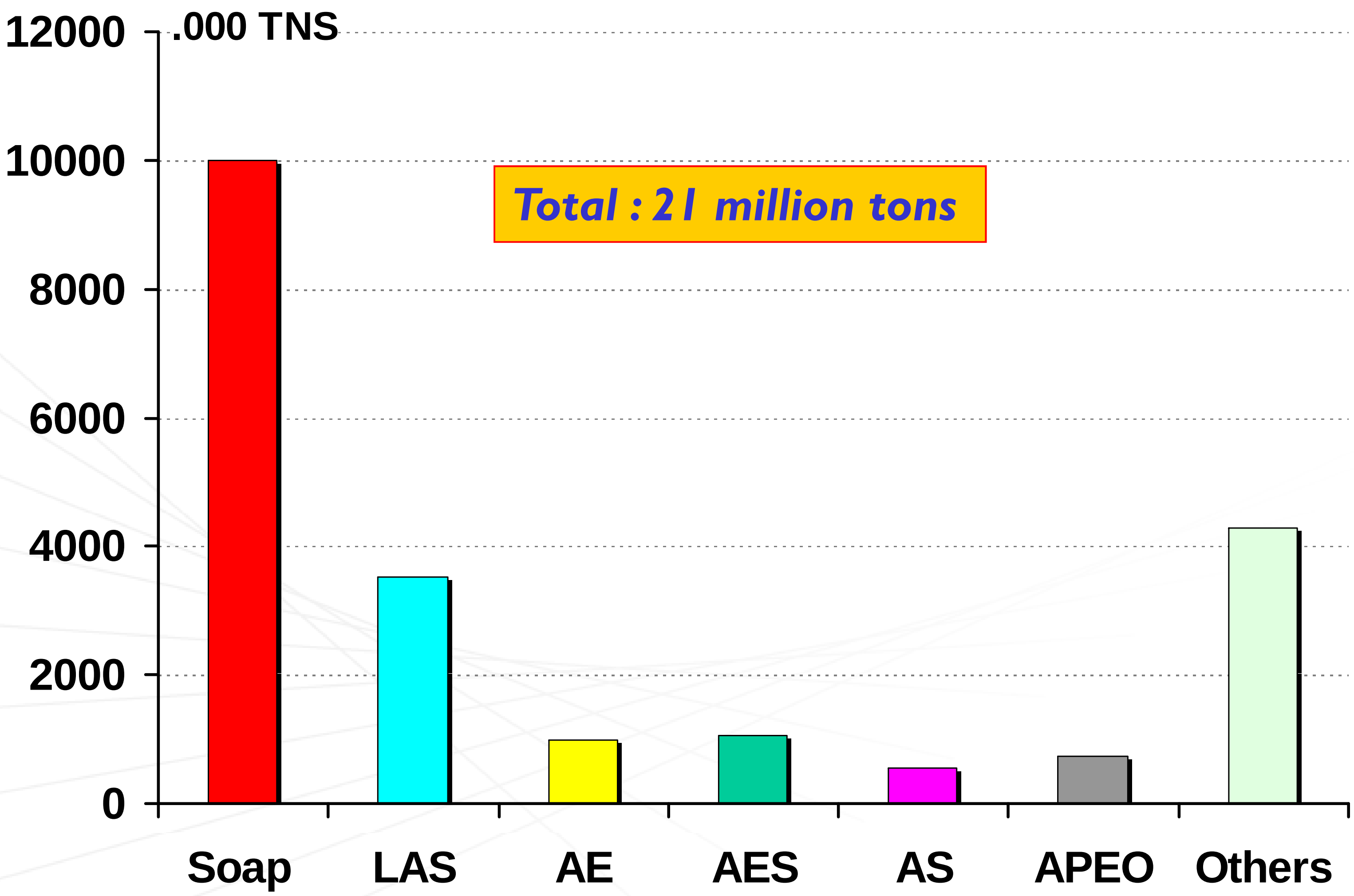




Heavy Duty Powders	- Regular	(HDP-R)	5 - 15 wt%
“ “ “	- Compact	(HDP-C)	5 - 15 “
“ “ “	- Tablets	(HDP-T)	5 - 15 “
Light Duty Powders (Fabric care)			10 - 20 “
Hand Dishwashing Liquids		(LDL)	0 - 25 “
Heavy Duty Liquids		(HDL)	0 - 25 “
Pastes & Gels (Dishwashing)			10 - 20 “
Hard Surface Cleaners			0 - 10 “
All Purpose Cleaners			0 - 5 “
I&I Cleaners			5 - 15 “

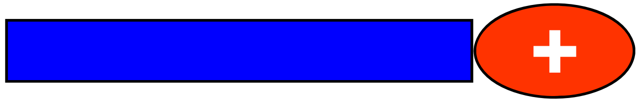
Consumption of Domestic Surfactants

Estimated World Surfactant Consumption - 2007



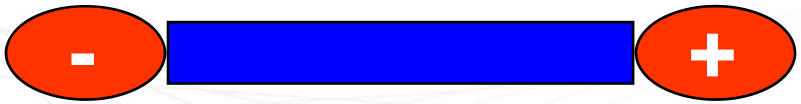
Surfactant Categories

Anionics: The Hydrophilic Moiety has a negative charge



Cationics : The Hydrophilic Moiety has a positive charge

Non-ionics : No specific charge in either moiety



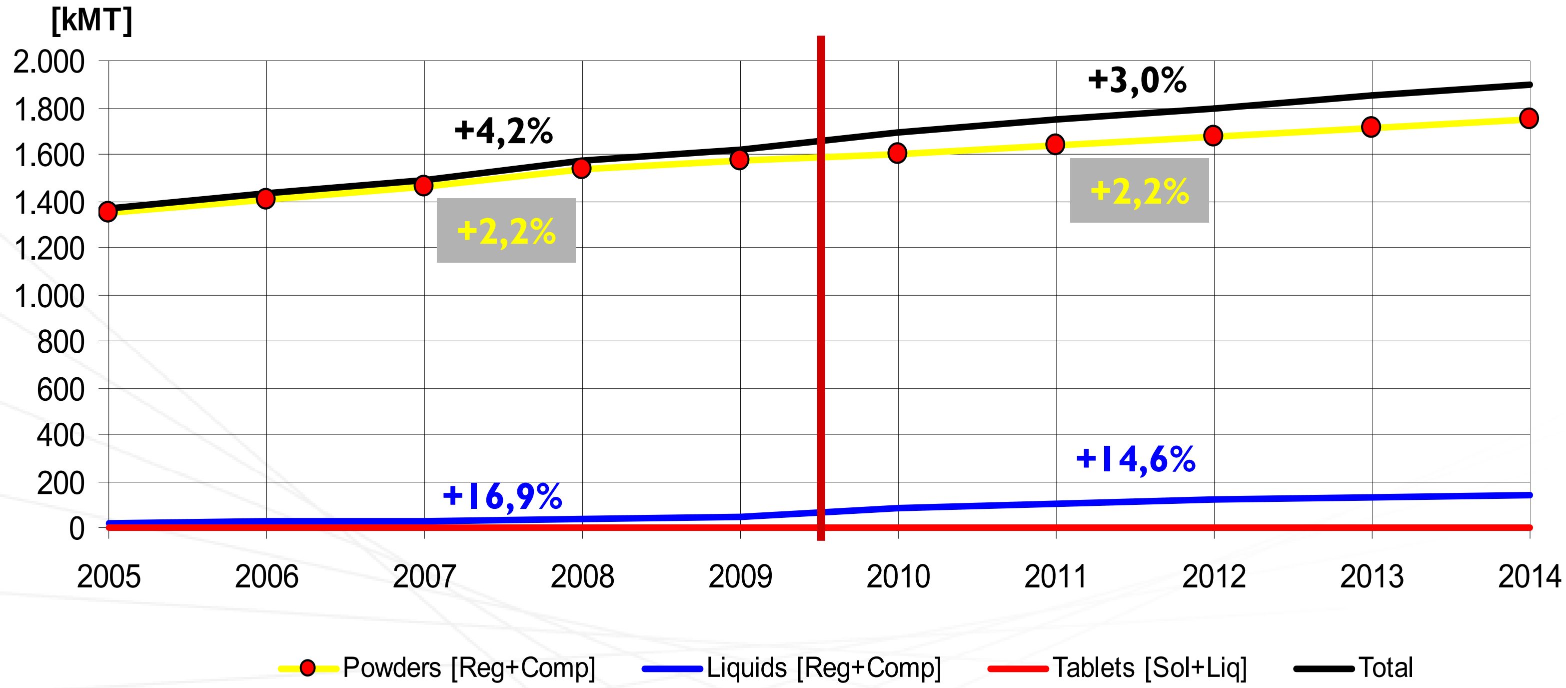
Amphoterics : Positive & Negative charges in the molecule

Properties of the surfactants can vary with:

- ***The length and the branched grade of hydrophobic group.***
- ***Nature of the hydrophilic group.***

Laundry Detergents Consumption in Latin America

In 2009, the Latin American Laundry detergents market accounts 1,6 MM MT.

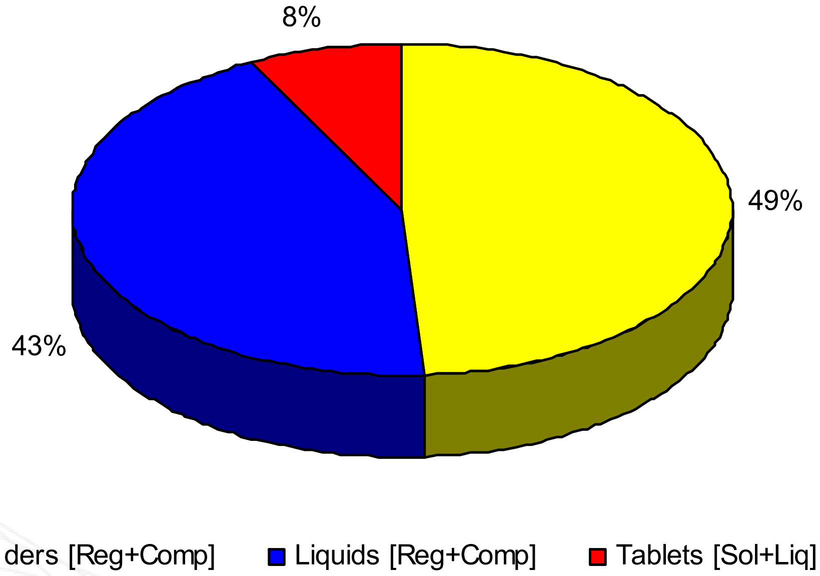


82% of the consumption is located on Brazil (47%), Argentina (16%), Colombia (11%), Venezuela (8%).

Source: Euromonitor

Laundry Detergents Consumption in W.E.

Laundry Detergents = 2,5 MM MT



For Laundry, 83% of the consumption was located on Germany (19%), Italy (17%), UK and France (16% each) and Spain (15%).

LAS Properties

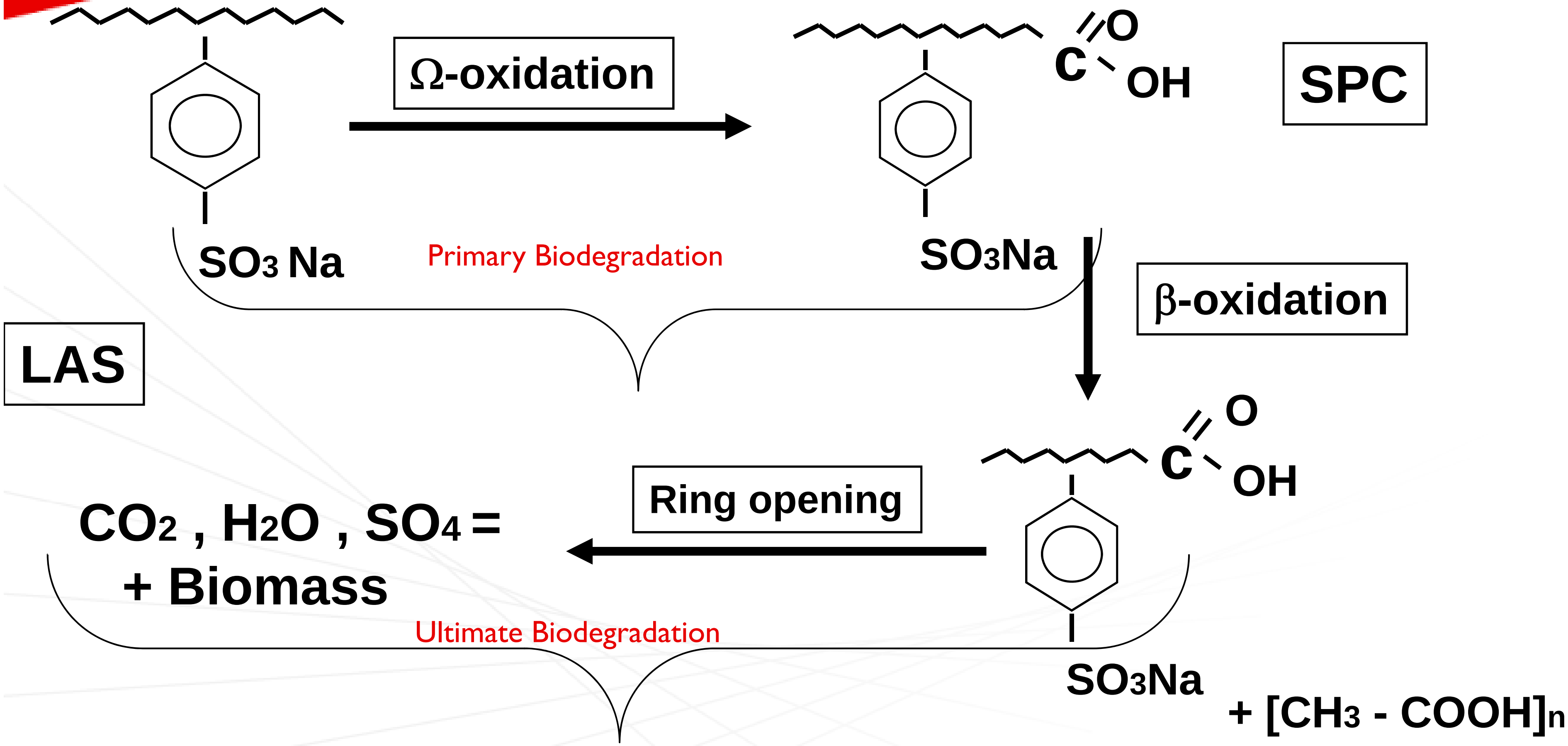
LAS Human & Enviromental risk assessment under HERA project
www.heraproject.com

Biodegradation

Biologically mediated process which results in the conversion of an organic chemical into organic and inorganic end products which are chemically distinct from the parent material.

- Aerobic Biodegradation is the most important mechanism for the total removal of chemicals in the environment
- It is nature's way of getting rid of wastes by breaking down organic matter
- As a result, the ability of a chemical to biodegrade aerobically is an indispensable element in the understanding of any risk posed by that chemical on the environment

LAS Biodegradation Pathway



Swisher R . D. in Surfactant Biodegradation (M.Decker ,N.Y.1987)
Huddleston R. et.al. Soap Cosmetics & Chem.Spec. 3/79
Schöberl P.et.al.Tenside Surf.Det. 1989,26,86
Cavalli L.et.al.,CESIO Congress,V4,448,Barcelona 1996

Biodegradation test

Summary of results for typical Cut ($C_{11.6}$):

Primary Biodegradation	
.-Screening test ,OECD 301-D	**>99%**
.-Confirmatory test,OECD 303-A	**>99%**
Ultimate Biodegradation	
.- Ready , OECD 301-B,D,E	**50 - 88%**
.- Inherent , OECD 302-A,B	**95 - 98%**
.- Simulation , OECD 303 -A	**>95%**
.- ^{14}C test	**>98%**

" LAS is a readily biodegradable surfactant "

European Commission DG - III , WRc Report EC-4294 , Feb.1997

Biodegradation test

Recent tests run according to the GLP principles, namely, CO_2 evolution test following OECD 301B (LAUS, 2005), DOC die-away test following OECD 301A (LAUSb, 2005) and mineralization under ISO 14593/1999 test (Lòpez et al., 2005)

LAS meets biodegradability requirements established on Detergent Regulation 648/2004

Aerobic Biodegradation in water

Field studies, carried out in some rivers under realistic environmental conditions specifically to measure in-stream removal kinetics of LAS, showed

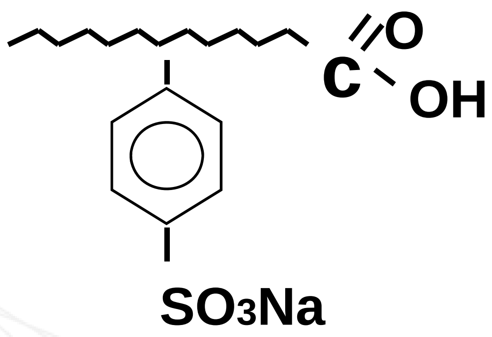
$t_{0.5}$ in the 1-3 h range

Therefore: kinetics are faster than those displayed in laboratory studies (Takada et al., 1992; Schröder, 1995; Fox et al., 2000)

This is due to the more favourable biodegradation conditions in the real environment vs. those reproduced in laboratory.

Biodegradation: Metabolites

The formation of persistent biodegradation intermediates can be excluded as demonstrated by high tier tests (Gerike et al., 1986; Moreno et al., 1991; Cavalli et al., 1996b).



SPC

Biodegradation intermediates, i.e. the sulpho phenyl carboxylates (SPCs), are not persistent and their toxicities are several orders of magnitude lower than that of the parent molecule (Kimerle et al., 1977).

Biodegradation test

Considering the absence of persistent metabolites and the relatively low toxicity of the transient degradation products, the rate of primary biodegradation, rather than that of the ultimate biodegradation is the relevant parameter for risk assessment purposes

SPC do not form foam since it is no longer a surfactant

Anaerobic Biodegradation

Laboratory screening and simulation tests (ECETOC, 1994; ERASM, 2007), which measure the ultimate biodegradation by determining the final gas production (CO2 and CH4) after about 2 months of incubation, LAS did not show any significant biodegradation (Steber et al., 1989; Steber, 1991; Federle et al., 1992; ERASM 2007; Gejlsbjerg et al., 2004; Garcìa et al., 2005).

LAS can biodegrade under methanogenic conditions, but low bioavailability in waste water treatment plant reactors is the main factor which in reality prevents any substantial biodegradation (Angelidaki et al., 2000a; Mogensen et al., 2003)

However, in oxygen-limited conditions, which occur in the real world, LAS biodegradation can initiate and then continue in anaerobic conditions (Larson et al., 1993; Leon et al., 2001, Gonzalez Mazo et al., 2010).

Environmental Relevance

In addition, the opinion of the Scientific Committee on Health and Environment Risks (SCHER), a committee of experts who serve an advisory role within the European Commission (EC), on the environmental risk posed by detergent surfactants that are poorly biodegradable under anaerobic conditions, such as LAS, is as follows:…"*A poor biodegradability under anaerobic conditions is not expected to produce substantial modifications in the risk for freshwater ecosystems as the surfactant removal in the STPs seems to be regulated by its aerobic biodegradability* "

This view is shared by the Industry (Erasm report; Tenside, 2008; Fraunhofer)

Environmental Relevance

The ERASM report concludes that:

"It is therefore concluded that anaerobic biodegradability as a strict pass/fail criterion is not in line with the environmental interpretation and significance that should be given to the lack of this property for surfactants. For surfactants used today in detergents, rapid aerobic biodegradation as well as their sorptive and ecotoxicological properties, are key to making a realistic assessment of environmental compatibility. If a surfactant is rapidly degradable under aerobic conditions, and its transitory presence in anaerobic environments does not affect the function and structure of that environment (e.g. it is not inhibitory), then its anaerobic degradability is of minor importance."

Aquatic toxicity

The toxicity database for LAS (Kimerle, 1989; SDA, 1991; Painter, 1992; IPCS, 1996) is very rich and well documented.

A comprehensive review of environmental information for the aquatic compartment that includes all data of the above mentioned literature is the BKH report (BKH, 1993). This report collects 749 records of toxicity data for LAS, specifically collated for an aquatic environmental risk assessment in the Netherlands (AISE/CESIO, 1995; Feijtel et al., 1995b; Van de Plassche et al., 1999a).

The database covers several taxonomic groups; intra- and inter-species variability is large, particularly in case of algae.

Acute, chronic and Model ecosystem studies are available.

Aquatic toxicity

Taxon	IC_{50}; EC_{50}; LC_{50} (mg/l) Geometric mean
Algae, IC_{50}	9.1 (n = 12, SD = ±3.9)
Invertebrate (*Daphnia m.*), EC_{50}	4.1 (n = 17, SD = ±2.0)
Fish (*Lepomis m.*), LC_{50}	4.1 (n = 12, SD = ±1.7)
Fish (*Pimephales p.*), LC_{50}	3.2 (n = 4, SD = ±1.6)

Species	End point	NOEC (mg/l) Geometric mean	Range (mg/l)
Chlamydomonas reinhardi, alga	growth	12 (1)	-
Chlorella kessleri, alga	growth	3.5 (1)	-
Microcystis spec., alga	population density	0.80 (4)	0.05-6.1
Plectonema boryanum, alga	growth	15 (1)	-
Scenedesmus subspicatus, alga	growth	7.7 (4)	0.8-105
Selenastrum spec., alga	population density	3.8 (9)	0.58-17
Ceriodaphnia spec., crustacean	reproduction	3.2 (1)	-
Daphnia magna, crustacean	mobility	1.4 (12)	0.3-6.6
Chironomus riparius, insectum	emergence	2.8 (1)	-
Paratanytarsus parthenogenica, insectum	growth	3.4 (1)	-
Brachydanio rerio, fish	mortality	2.3 (1)	-
Pimephales promelas, fish	mortality and others	0.87 (14)	0.5-4.8
Poecilia reticulata, fish	reproduction	3.2 (1)	-
Oncorhynchus mykiss, fish	-	0.34 (7)	0.23-0.89
Tilapia mossambica, fish	reproduction	0.25 (1)	-

3h EC_{50} of LAS for microorganisms present in the aerobic activated sludge was experimentally measured at 550 mg/l_(Verge et al., 1993; Verge et al., 1996).

A NOEC value of 35 mg/l, normalised to the $C_{11.6}$LAS structure, was found for *Pseudomonas putida* after a growth inhibition test (Feijtel et al., 1995b).

The microbial population present in the STP activated sludge digesters was not found to be inhibited even by a high and atypical concentration (30 g/kgdw sludge) of LAS in sludge (Berna et al., 1989).

Bioconcentration

The purpose of the estimation of bioconcentration is to assess whether there is any potential for the chemical to accumulate in organisms to a high degree and hence, for further transfer up the food chain.

An in depth research project on bioconcentration of surfactants was completed and concluded that LAS is not bioaccumulative. The bioconcentration potential of LAS is low and is decreased by environmental processes such as biodegradation and absorption (Tolls, 1998).

Results confirmed recently by Dyer et al. (2008) and ERASM reports (www.erasm.org/study.html)

Bioconcentration potential estimation: i) ca. 87 l/kg for commercial LAS mixture (C11.6 alkyl chain length); ii) ca. 22 l/kg for LAS in river water (C10.8 alkyl chain length).

Therefore, LAS does not accumulate in living organism

Endocrine Disruptor Effects

LAS was also investigated to check whether it could be an endocrine disruptor, using an estrogens-inducible yeast screen (Routledge et al., 1996; Navas et al., 1999) and the vitellogenin assay with cultured trout hepatocytes (Navas et al., 1999).

LAS as well as its biodegradation intermediates, Sulpho Phenyl Carboxylates (SPC), did not display any estrogenic effects.

CEPSA

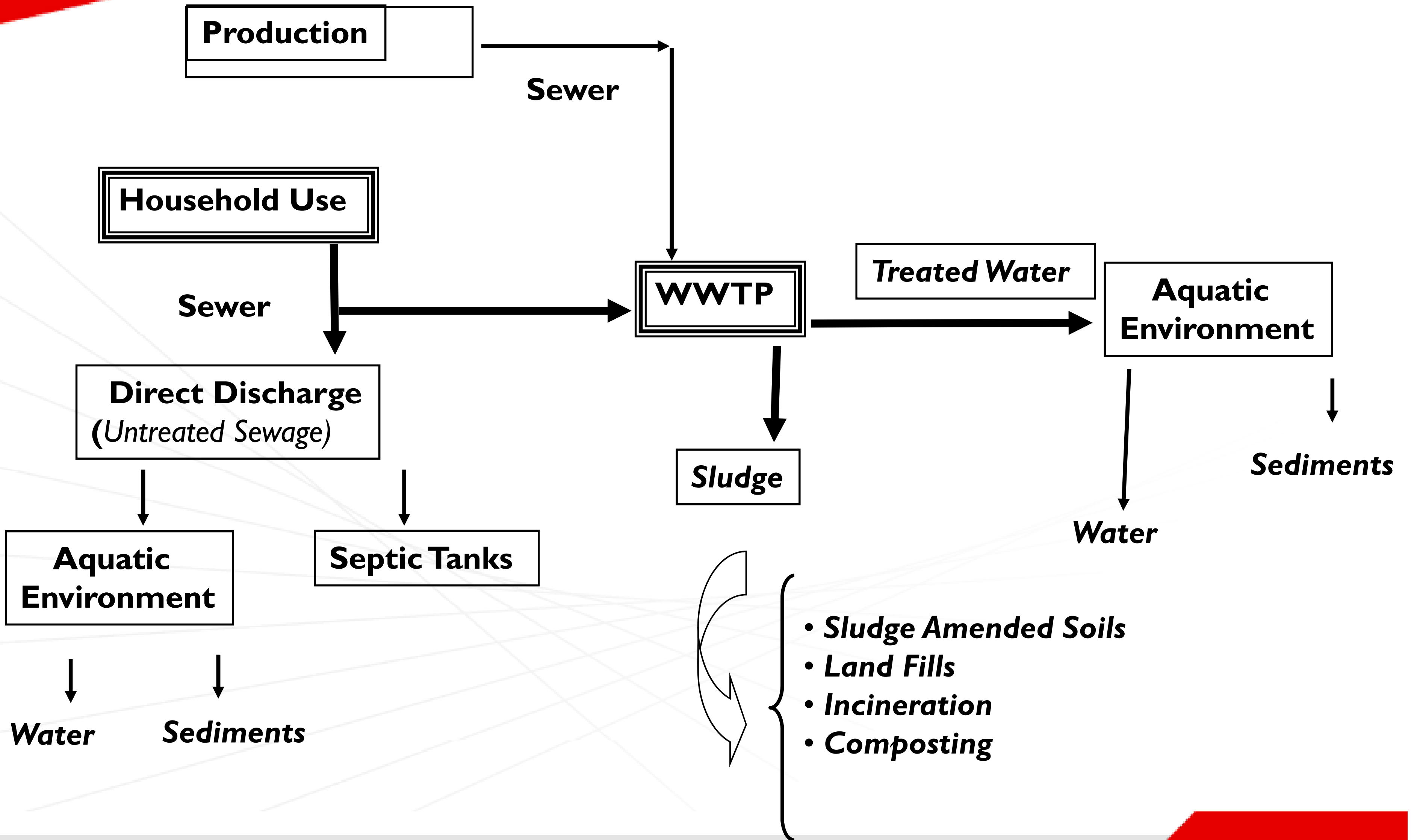
Conclusion

LAS is not classified as dangerous for the environment (EU Dangerous Substances Directive because :

a) is a readily biodegradable surfactant
b) has a low aquatic toxicity level (>1mg/l)
c) does not bioconcentrate (BCF < 100)

Environmental & Human Safety

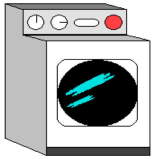
Fate and removal of LAS in the Environment



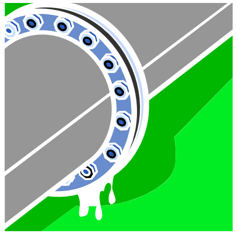
Monitoring of LAS in the Environment.

LAS	Results	References
Effluent (µg/l)	as-STP: 8-220 (range) as-STP: 2-273 (range) as-STP: 42.8 (arithmetic mean) as-STP: 1.3-2.9	Feijtel et al., 1995b Holt et al., 2003 Matthijs et al., 1999 Sanderson et al., 2006
River water (µg/l)	down as-STP: <2-47 (range) down as-STP: 14.2 (arithmetic mean) down as-STP: 0.3-3.8	Feijtel et al., 1995b Matthijs et al., 1999 Sanderson et al., 2006
Ground water (µg/l)	0-3	Field et al., 1992
Anaerobic sludge ($g/kg_{dw\ sludge}$)	5.56 (median 50^{th} percentile) 0.49-15.07 (5^{th} to 95^{th} percentile)	Schowanek et al, 2008
River sediment ($mg/kg_{dw\ sed.}$)	<1-5.3 (typical range) 2.9 (arithmetic mean)	Cavalli et al., 2000
Soil (mg/kg_{dw} soil)	0.7-1.4, measured at harvest time (30 d) <1, typical agricultural value	Mortensen et al., 2001 Carlsen et al., 2002

Fate of LAS in the Environment

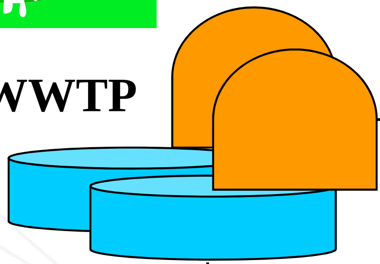


LAS in Raw Sewage : 1-15 mg/l



Biodegradation in Sewers : 50%

WWTP



Removal through Biodegradation in WWTP : >85%
“ “ Precipitation - Adsorption: < 15%
Total Removal : > 99%

LAS in Sludge : <1 - 10 g/ Kg

LAS in Treated Water : < 0.1 mg/l
LAS in Receiving Waters: <0.002 - 0.05 mg/l

Biodegradation in Sludge Amended Soils : >95%
“ during Composting : > 99%
LAS in Sludge amended soils : ~ 1 mg/Kg

Removal in Activated Sludge WWTP

The following proportions are based on as-STP mass balance studies: 80-90% degraded, 10-20% adsorbed onto sludge and about 1% released to surface waters (Berna et al., 1989; Painter et al., 1989; Cavalli et al., 1993; Di Corcia et al., 1994).

Fate of LAS in the Environment.

Removal

	Half Life ($t_{0.5}$)
Sewers	10 - 12 hrs
In stream	3 - 12 "
Biological Treatment	1 - 2 "
Sludge	3 - 24 months
Soils	10 - 33 days
Composting	6 - 14 "

Figge K. et.al. NATEC Report ,1991
Marcomini A. et.al. J.Env. Qual., 18 (1989), 523
Berna J.L. et.al, Tenside Surf.Det., 26 (1989) 26, 101

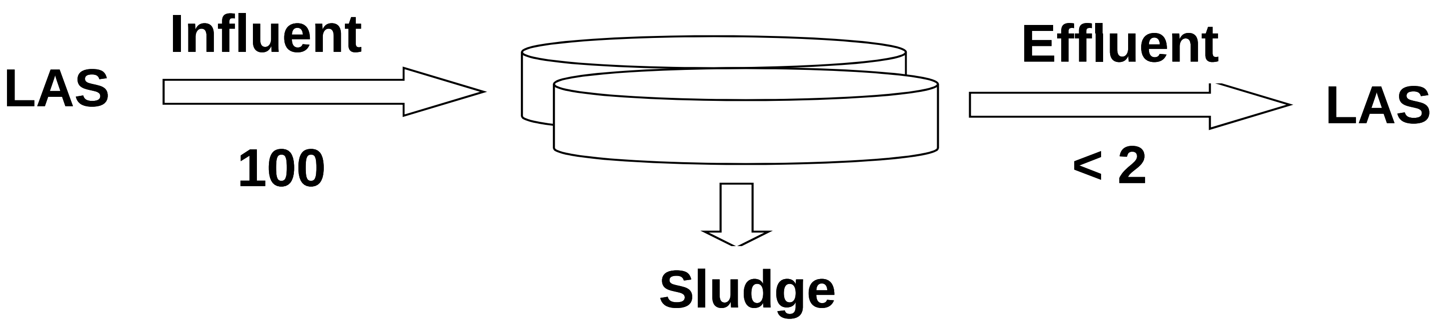
Surfactant Biodegradation in Sewers

Surfactant	% (Range)
LAS	50 (10 - 68)
AE	42 (28 - 58)
AES	11 (0 - 40)
AS	55 (18 - 85)

Limelette III ,AISE -CESIO Workshop , 1995

Fate of LAS in the Environment.

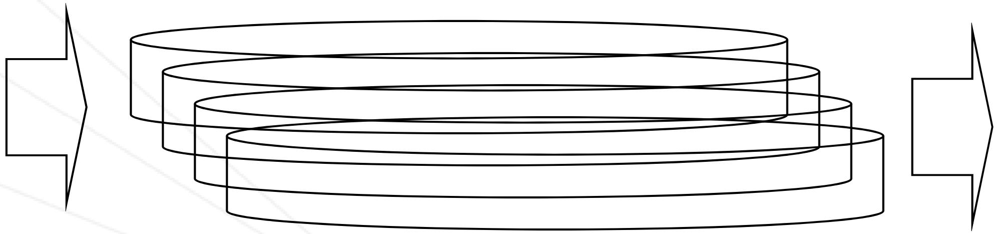
Removal in AS-WWTP



Total Removal	**> 98%**
Physical Removal (Precipitation/Adsorption) **(Water Hardness Dependent)**	**15 - 25 %**
Biological Removal (Mineralization)	**75 - 85 %**
Half life in the Biological System	**1 - 2 hrs**

Berna J.L. et. al. Tenside Surf. Det. 26 (1989),101
Painter H. et. al.Tenside Surf. Det. 26 (1989),108
Cavalli L. et. al. Env.Tox.Chem., 12 (1993), 1777

LAS Removal in Lagoons Treatment



Total Removal > 97 %
Biodegradation > 83%

Moreno A.. et.al., CESIO World Surfactant Congress, London,1992

Biodegradation in Septic Tanks Systems

LAS biodegraded extensively in subsurface soil system.
No migration to drinking water aquifers was detected.

US SDA Investigation of an On Site Waste Water Treatment System in Sandy Soil.,1998

Removal. Sludge Anaerobic Treatment

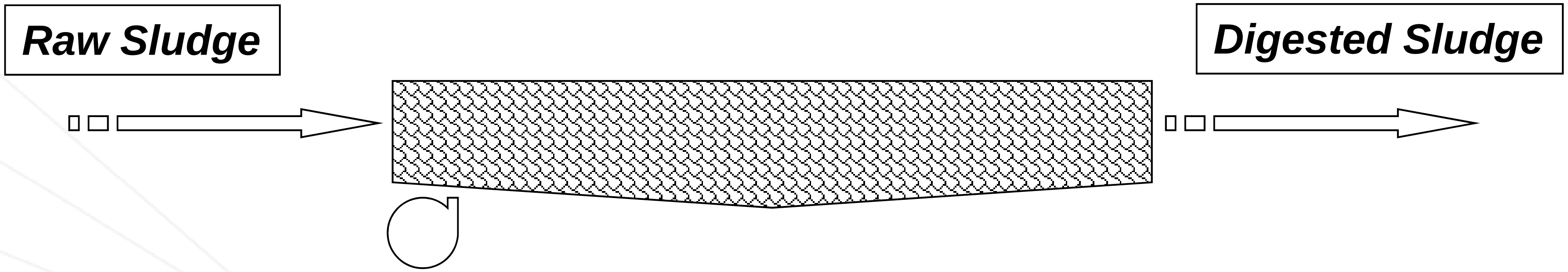
LAS Removal: 10 - 20% on mass basis

- **LAS degrades under strict anaerobic S-limiting conditions**
- **LAS is removed in UASB anaerobic reactors (40 - 90 % in 15 days)**

Berna J.L. et.al.Tenside Surf. Det. 26 (1989), 101
Prats D. et.al.Water Research, 31 (1997),1925
AISE - CESIO Report on Anaerobic Biodegradation of Surfactant, 1999
Denger K. et.al. J.Appl. Microbiology, 86 (1999),165
Sanz J.L. et.al.,Proceedings CID meeting, Napoli 1999
SPT Workshop with EPA, Copenhagen 1999
Angelidaki I. et. al. Biodegradation 2 (2000), 377-383

Fate of LAS in the Environment.

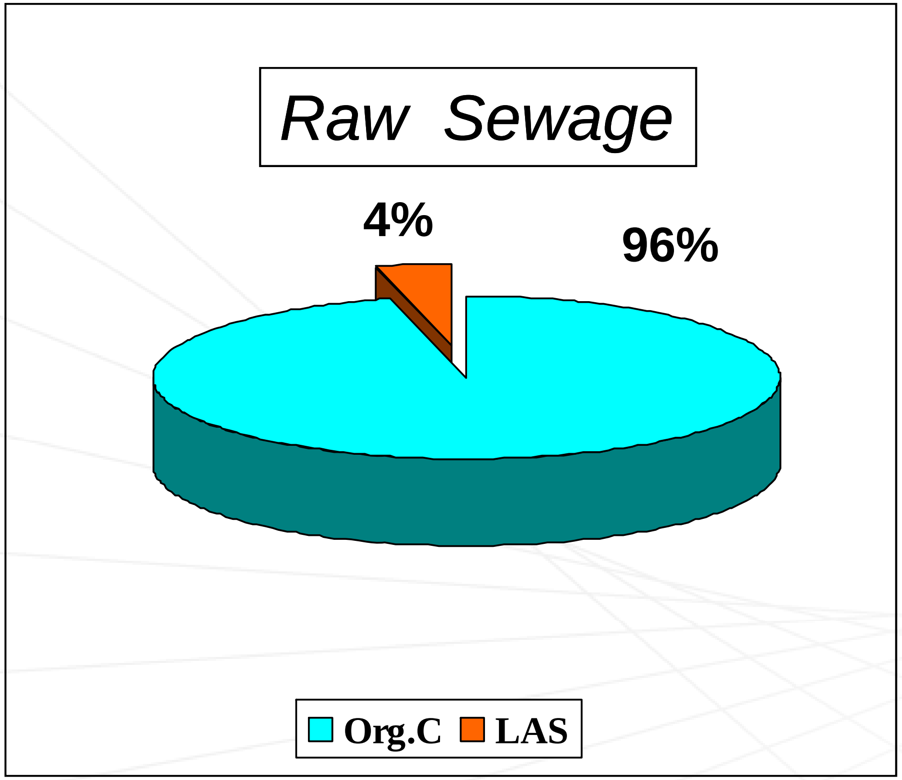
Removal. Sludge Aerobic Treatment

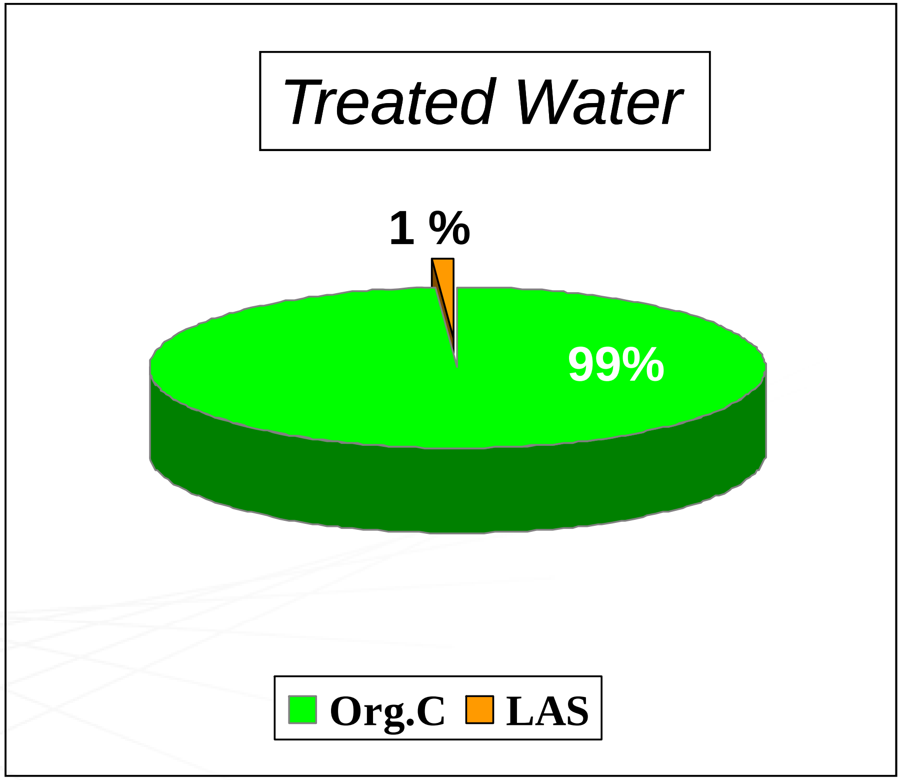


LAS Removal > 95%

Berna J.L. et.al. Tenside Surf. Det. 26 (1989),101

LAS Contribution to Total Organic Carbon Content





Berna J.L. et.al. 3rd CESIO World Congress, London 1992

LAS versus BOD Removal

	% LAS	% Org.C
WWTP (Act.Sludge)	96 - 98	88 - 93
Composting	96 - 99	30 - 40
Lagoons	95 - 97	85 - 87

Moreno A. et.al. CESIO World Congress,London 1992

Biodegradation in Sludge Amended Soils

•The most reliable results in the laboratory were obtained by investigating mixtures of sludge and LAS-spiked soils using 14C materials, measuring ultimate biodegradation. LAS mineralization rates corresponding to $t_{0.5}$ = 13-26 days (Figge and Schöberl, 1989) and t0.5 = 7.0-8.5 days (Gejlsbjerg et al., 2001) were estimated.

•Mineralization with $t_{0.5}$ = 2.1-2.6 days was obtained after a lag time of 1.9-2.5 days at 10 mg/kgdw (Gejlsbjerg et al., 2003).

•Laboratory sludge-soil mixtures with 14C-labelled LAS at concentrations in the µg/kgdw soil range, corresponding to predicted steady concentrations (at least after a waiting period of 30 days from sludge application) of the surfactant in sludge-amended soil, were also investigated (Gejlsbjerg et al., 2004). After relative long lag times (ca. 2 weeks), LAS was mineralized rapidly and extensively showing two phase kinetics: a first rapid mineralization (t0.5 = ca. 2 days) followed by a slow mineralization phase (t0.5 = 7.9 days), the latter likely governed by sorption and desorption processes in the soil.

•In the laboratory tests it was shown that for soil spiked with aqueous LAS and LAS-spiked sewage sludge, the disappearance (primary biodegradation) of the surfactant was more than 73% after 2 weeks (Elsgaard et al., 2001b).

•A soil mesocosm study showed that the primary degradation of LAS was rapid with t0.5 of 1-4 days (Elsgaard et al., 2003).

A field study, at sludge application rates close to those recommended in agriculture (equal or below 5 tdw/ha/y), estimated t0.5 values in the range of 3-7 days (Küchler et al., 1997).

Accurate data for degradation of LAS in sludge-amended soil under realistic field conditions were reported by Mortensen et al., 2001. Its degradation in soil increased by the presence of crop plants with soil concentrations decreasing from 27 mg/kgdw to 0.7-1.4 mg/kgdw soil at harvesting time after 30 days (t0.5 <4d).

Biodegradation in Sludge Amended Soils

Considering the above available field data**, a conservative protective primary biodegradation half-life of 7 days in agricultural soils was considered in the HERA risk assessment.**

Biodegradation in Sludge Amended Soils - “Plant Metabolism Box” - ^{14}C LAS

Soils amended with sludge containing ^{14}C LAS . Biodegradation process monitored through radioactivity in a environmental chamber.

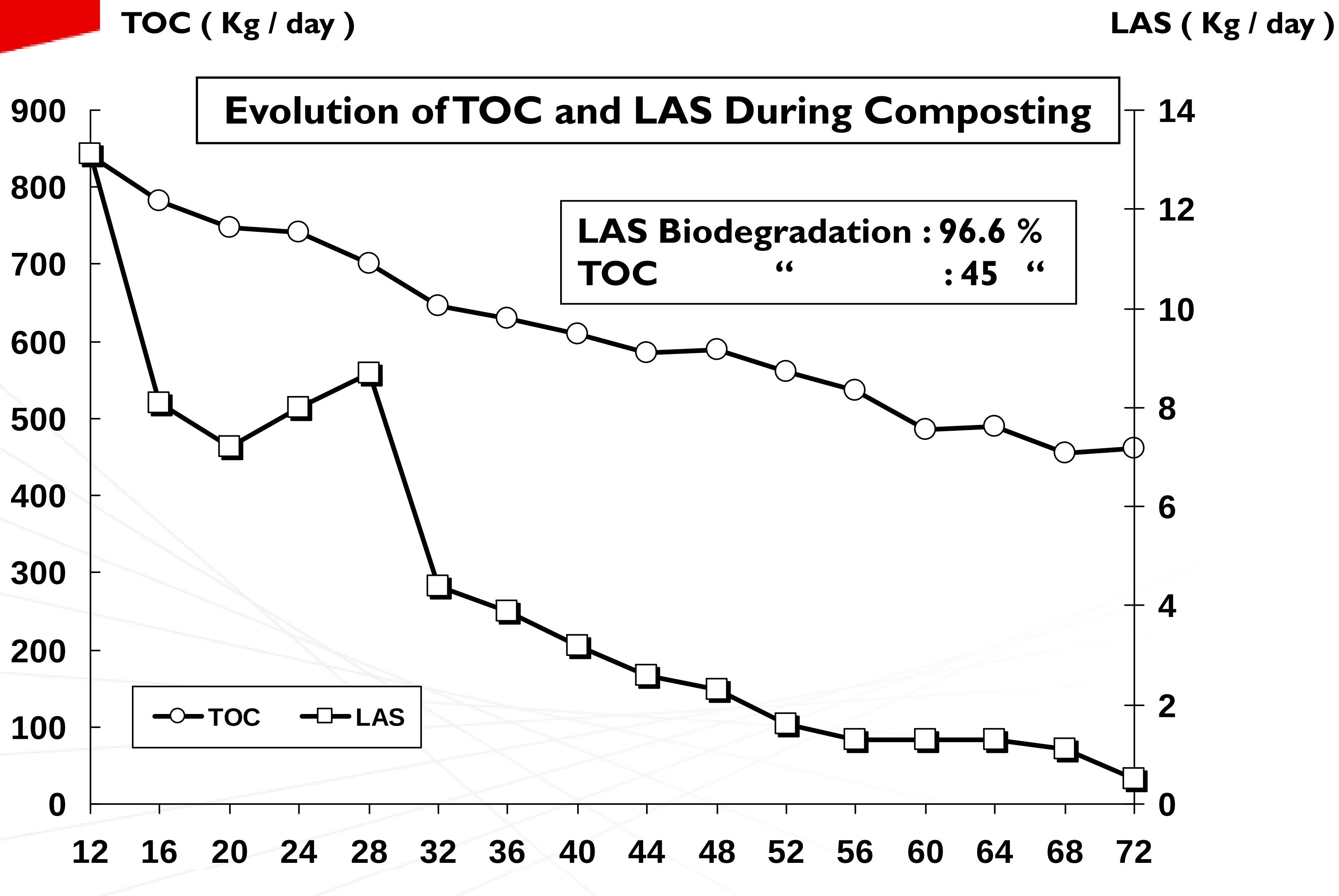
Radioactivity Recovery : >98% :

.- 64 - 72 % as ^{14}C - CO_2 in the atmosphere
.-18 - 27 % in the soil core
.- 6 - 7 % in the biomass
.- 1 % in the leaching water

Intact LAS was only found (1 - 2 %) in the soil core.

Figge K. et.al. Tenside Surf.Det. 26 (1989), 122

Fate of LAS in the Environment.



Prats D. et.al. SPT Workshop with EPA, Copenhagen 1999; TENSIDE

Biodegradation data for Risk Assessment Purposes

LAS	Protocol	Results	References
Screening, confirmatory	OECD 301 D OECD 303 A	>99 (% primary biod.)*	EU Commission, 1997
Ready test	OECD 301 A, B, D, E, F ISO 1493/1999	Readily biodegradable >70 (% DOC removal) >60 (% CO_2 evolution) >60 (% O_2 uptake)	EU Commission, 1997 Ruffo et al., 1999 Temmink et al., 2004 LAUS, 2005a-b Lòpez et al.,2005
Inherent test	OECD 302 A, B	95-98 (% DOC removal)	EU Commission, 1997
Simulation test	OECD 303 A	80->95 (% DOC removal)	EU Commission, 1997
Biodegradation rate in activated sludge	Die-away	$t_{0.5}$ = 0.6-0.7 h (prim. biod.) $t_{0.5}$ = 1.3-1.4 h (ultim. biod.)	Federle et al., 1997
Biodegradation rate in river water	Die-away Die-away River monitoring	$t_{0.5}$ = 12 h (prim. biod.) $t_{0.5}$ = 18 h (ultim. biod.) $t_{0.5}$ = 1-3 h (prim. biod.)	Itrich et al., 1995 Itrich et al., 1995 Fox et al., 2000
Anaerobic biodegradation	ECETOC Research study	ca.0 (% ultim. biod.) 5-44 (% prim. biod. in UASB reactors)	AISE/CESIO, 1994 Mogensen et al., 2003
Biodegradation rate in soil	Field study Laboratory study	$t_{0.5}$ = 1-7 d (prim. biod.) $t_{0.5}$ = 2-26 d (ultim. biod.)	Küchler et al., 1997 Elsgaard et al., 2003 Figge et al., 1989 Gejlsbjerg et al., 2001, 2003, 2004

Hazard (Peligro) and/y Risk (Riesgo)

What is the 'hazard' of a substance?

Some, or all, of its **intrinsically harmful properties**, including

- toxicity and ecotoxicity;
- carcinogenicity, mutagenicity….;
- flammability, corrosivity….;
- irritancy, sensitisation potential
- ……

What is the 'hazard' of a substance ?

…..and properties which are not in themselves harmful but may increase the hazard of other properties, including:

- persistence;
- bioaccumulation potential.

Hazard and Risk

What is ‘risk’?

Risk is an **expression of the probability**, the possibility or the likelihood **that hazardous properties**, combined with exposure, **will cause harmful effects.**

Therefore risk assessment involves an estimate of probability or chance, based on the co-incidence of a hazard and some kind of exposure to that hazard.

Hazard and Risk

¿Cómo se expresa el Riesgo de una Sustancia Química ?

Comparing PEC and PNEC

PEC : Predicted Environmental Concentration
Margen de Exposición

PNEC : Predicted No Effect Concentration
Nivel al cual no se observan effectos negativos (NOAEL)

PEC / PNEC > 1 = Riesgo !
PEC / PNEC < 1 = No Riesgo

Terrestrial

A large number of LAS toxicity data, both in laboratory and field, are available for the terrestrial environmental risk assessment. Data refer to the effects of LAS on soil organisms, namely toxicity to soil plants, soil fauna, soil micro-organisms and microbial soil processes (Kloepper-Sams et al., 1996; Jensen, 1999; Jensen et al., 2001; Holmstrup et al., 2001a; Elsgaard et al., 2001a, Jensen et al., 2008).

Chronic Toxicity Data

Taxon	Range ($mg/kg_{dry\ soil}$)
Plants, NOEC or EC_{10}	52 - 200 (12)
Soil fauna, NOEC or EC_{10}	27 - 320 (9)
Micro-organisms, EC_{10}	<8 - >793 (10)

LAS Ecotoxicity.

Sediments

Species	Most sensitive end point	NOEC ($mg/kg_{dw\ sed.}$)	References
Chironomus riparius	reproduction, survival	319 362, 537	Pittinger, 1989 Kimerle, 1989 Mäenpää and Kukkonen, 2006
Unio elongatulus *Anodonta cygnea*	survival survival	>200 >200	Bressan et al., 1989
Lumbriculus variegatus	survival, reproduction, growth	81	Comber et al., 2006
Caenorhabditis elegans	egg production	100	Comber et al., 2006

Risk Assessment under HERA project

LAS	PEC	PNEC	PEC/PNEC
Water, mg/l	0.047	0.27	**0.17**
Soil (30 d), $mg/kg_{dw\ soil}$	1.4	35	**0.04**
Sludge, $g/kg_{dw\ sludge}$	5.56 (50th percentile 15.07 (95th percentile)	49	**0.11** **0.31**
Sediment, $mg/kg_{dw\ sed.}$	5.3	8.1	**0.65**
STP, mg/l	0.27	3.5	**0.08**

PEC: Predicted Environmental Concentration. PEC values were estimated based on monitoring data for each environmental compartment

PNEC: Predicted Non Effect Concentration. PNEC values were based on chronic effects data.

This assessment shows that the use of LAS results in risk characterisation ratios (PEC/PNEC) less than one.
Therefore, it was concluded that the ecotoxicological parameters of LAS have been adequately and sufficiently characterized and that the ecological risk of LAS is judged to be low.

LAS Risk Assessment. www.heraproject.com

European Risk Assessment of Major Surfactants

Surfactants studied in NL for the aquatic environment

LAS (Data Normalized to $C_{11.6}$ Na LAS)
AE (" " " $C_{13.3}$ $EO_{8.2}$)
AES (" " " $C_{12.5}$ $EO_{3.4}$)
Soap

Other Risk Assessment Studies

Aquatic Env.	PEC(mg/l)	PNEC(mg/l)	PEC/PNEC
Europe	*1-15*	*250*	*<0.1*
The Netherlands	*3.7*	*250*	*<0.02*
Denmark	*<6*	*250*	*<0.03*

Feijtel T. et.al. Report 679101025 , RIVM-NVZ,1995
Feijtel T.et.al. SPT Workshop with EPA,Copenhagen,April 1999

Other Risk Assessment Studies

Risk Assessment of Surfactants in Surface Waters

Ingredient	PEC	PNEC	PEC / PNEC
	.....(mg/l)....		
LAS	3.7	250	<0.02
AE	0.5	110	<0.01
AES	1.2	400	<0.01
Soap	20	27	0.74

"From the ratio between the PEC and the PNEC it can be concluded that the risk for LAS,AE and AES is low: PEC/PNEC ratios are < 0.02..."

Environmental Risk Characterisation of 4 major surfactants used in The Netherlands , 1995

Feijtel T. et.al. Report 679101025, RIVM - NVZ , 1995

Other Studies

"LAS must be regarded as one of the most intensely investigated environmental chemicals. ......we are dealing with a basically environmentally compatible surfactant. ....no detrimental accumulation is recognisable in the various environmental compartments"

International Status Seminar "LAS in the Environment" Aachen (D), 1988

"As far as LAS,AE and AES are concerned there is a good margin of comfort in the results of the Risk Assessment in The Netherlands. Degradation of these surfactants is faster than the BOD and provides no cause for concern over breakdown residues".

Environmental Risk Assessment of Detergent Chemicals.Limelette III,1995

CEPSA

Other Risk Assessment Studies

"As far as LAS,AE and AES are concerned there is a good margin of comfort in the results of the Risk Assessment in The Netherlands.
Degradation of these surfactants is faster than the BOD and provides no cause for concern over breakdown residues".

Environmental Risk Assessment of Detergent Chemicals.Limelette III,1995

"Even at a concentration of LAS in sludge equal to the highest observed in Denmark,LAS is not predicted to cause a problem when half - lives are less than 25 days ,provided that less than 8 tons of sludge per hectare per year are applied."
"PNEC of LAS in soil,substantiated by a great deal of data ,is 5.2 mg/Kg"
"No effects in soil field studies have been observed at LAS concentrations below 5 - 15 mg/Kg "

SPT Workshop with EPA ,Copenhagen 1999

Human Risk Assessment

LAS is :

.- Rapidly and Completely excreted following single oral dose.

.- Not substantially absorbed (< 0.01 %) percutaneously by humans

.- Not Classified as CMT (Carcinogenic, Mutagenic, Teratogenic).

In view of the extensive database on toxic effects, the low exposure values calculated and the resulting large Margin of Exposure described above, it can be concluded that use of LAS in household laundry and cleaning products raises no safety concerns for the consumers.

Environmental & Human Safety of Major Surfactants. The Soap & Detergent Association - New York 1991
Hera report. See www.heraproyect.com

European Life Cycle Inventory of Major Surfactants

" Based on the findings of this study , no technical or scientific basis exists to support a general environmental superiority claim ,either for an individual surfactant or for the various options for sourcing from petrochemical , oleochemical or agricultural feedstocks and minerals "

Tenside Surf.& Det. 1995 ,2, 32

Conclusion

LAS is among the most comprehensively tested chemicals

The recognition of its environmental safety is a victory of science over speculation..

After more than 40 years of world wide use , no other surfactant can match the safety credentials of LAS

Occurrence of Foam in the Tiete River

Background

- Occurrence of foaming episodes in Tiete River when passing by Pirapora do Bom Jesús since more than 30 years ago.

- Detergents are accused of being behind the foaming contamination affair

- Petresa report 13/2006: "*FORMACIÓN DE ESPUMAS EN EL RÍO TIETÉ: ANÁLISIS Y CONCLUSIONES*

  Monitoring Campaings in 2003, 2004 y 2005 sponsored by CETESB

Tiete River

Sampling Points

Tiete River

Sampling Points

-Ponte de Bandeiras, na Av. Santos Dumont

-Ponte dos Remedios, na Av. Marginal

-Reservatorio Edgard de Souza

-Reservatorio Pirapora

Tiete River

Results

- MBAS (ppm) in 2005

Punto de muestreo	*Enero*	*Marzo*	*Mayo*	*Julio*	*Septiembre*	*Noviembre*
Punto 1	1.72	1.44	1.76	3.68	2.8	2.32
Punto 2	2.7	0.76	3.24	5.1	3.32	3.72
Punto 3	0.83	3.28	4.12	3.92	2.6	4.04
Punto 4	1.02	1.8	2.95	3.08	2.96	3.12

MBAS (Methylene Blue Active Substances). It estimates the presence of anionic surfactants, mainly: LAS, AES and AS (present in personal care products as well as in detergents)

MBAS in the 1.0- 5.0 mg/l range. These concentrations are typical of direct discharges

Tiete River

Results

•Dissolved O2 (mg/l)

Punto de muestreo	*Enero*	*Marzo*	*Mayo*	*Julio*	*Septiembre*	*Noviembre*
Punto 1	<0.1	0	0.1	0	0.4	0.2
Punto 2	<0.1	0	<0.1	0	0.3	<0.07
Punto 3	<0.1	<0.1	<0.1	<0.1	0.4	0.2
Punto 4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.07

Anoxic Conditions. No apt either for aquatic living organisms or for aerobic micro organisms responsible for natural biodegradation processes (main mechanism behind the rivers self-depuration capacity)

Tiete River

Results

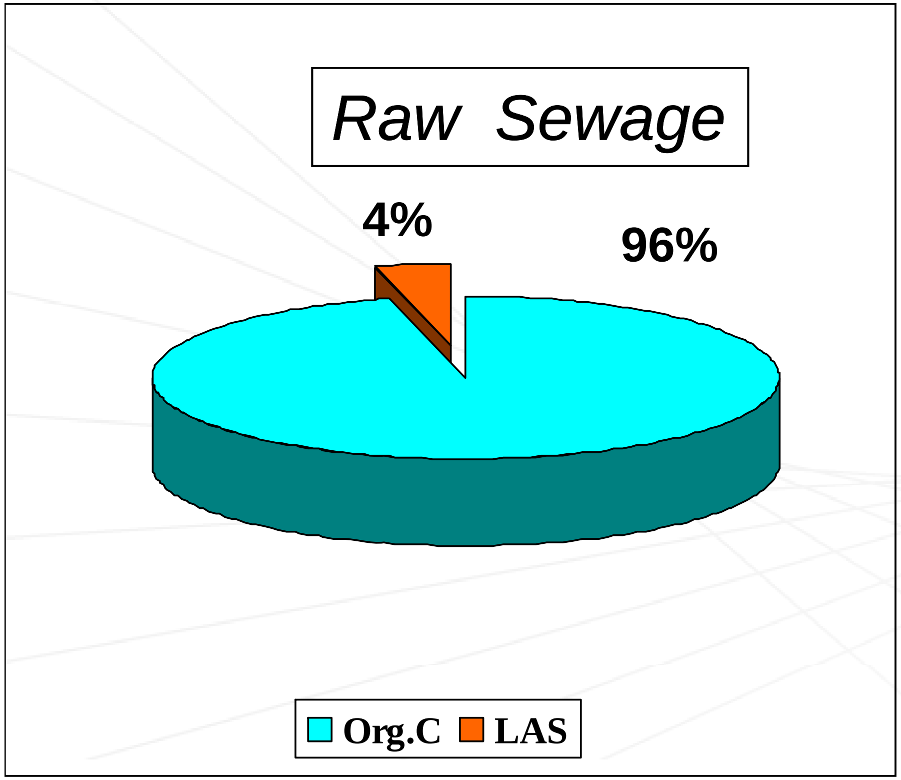
•DBO_5, DQO (mg/l)

PUNTO 1	Enero	Marzo	Mayo	Julio	Septiembre	Noviembre
DBO	22	20	38	44	43	23
DQO	81	73	105	156	123	81
DBO/DQO	**0,27**	**0,27**	**0,36**	**0,28**	**0,35**	**0,28**
PUNTO 2	Enero	Marzo	Mayo	Julio	Septiembre	Noviembre
DBO	29	18	43	380	34	40
DQO	120	125	129	1980	102	110
DBO/DQO	**0,24**	**0,14**	**0,33**	**0,19**	**0,33**	**0,36**
PUNTO 3	Enero	Marzo	Mayo	Julio	Septiembre	Noviembre
DBO	14	28	42	41	27	40
DQO	85	70	85	108	72	105
DBO/DQO	**0,16**	**0,40**	**0,49**	**0,38**	**0,38**	**0,38**
PUNTO 4	Enero	Marzo	Mayo	Julio	Septiembre	Noviembre
DBO	12	12	26	30	22	25
DQO	51	50	66	78	63	78
DBO/DQO	**0,24**	**0,24**	**0,39**	**0,38**	**0,35**	**0,32**

Tiete River

Results

Most sampling points have DBO/DQO ranging from 0.2-0.4, indicating the presence of recalcitrant OM. The river is therefore enriched in poorly biodegradable matter



	% LAS	% Org.C
WWTP (Act.Sludge)	96 - 98	88 - 93
Composting	96 - 99	30 - 40
Lagoons	95 - 97	85 - 87

Tiete River

Results

Nitrogen Compounds

- Ammoniacal N is proportional to organic contamination
- Under aerobic conditions, OM and Ammoniacal N are transformed into nitrates and nitrites.
- In Tiete, N is present in form of Ammoniacal salts as a consequence of the limited O2 availability

Therefore, the type of N-compounds indicates lack of oxygen

Tiete River

Results

Conductivity

According to EPA[1], in US Rivers 50 – 1500 µS/cm are the common and150-500 µS/cm are considered adequate for fishes and macroinvertebretes. Values detected at Tiete Rives were in the 250-750 µS/cm range.

[1] http://www.epa.gov/owow/monitoring/volunteer/stream/vms59.html

Tiete River

Results

Foaming

• It is provoked by substances capable of lowering the water surface tension yielding to water/air emulsion known as foam.

•Foaming might be formed:

- Anthropogenic Surfactants
- •effluents from paper and leather industries
- Humic acid, Proteins,etc.
- Natural surfactants associated to biological processes

• There are examples of naturally-ocurring foaming phenomena

- Ontario lake: Algae and plants cell material decompose yielding foam.
- N2 unbalance. Filament Microorganisms induce the formation of foam
- Rhine River. *Ranunculus fluitants undergoes biodegradation yielding saponines*

Occurrence of Stable Foam in the Upper Rhine River Caused by Plant-Derived Surfactants

Environ. Sci. Technol., 2002, 36 (15), pp 3250–3256
DOI: 10.1021/es025532p
Publication Date (Web): July 3, 2002

Abstract

For 30 yr, a persistent foam cover has been observed during the summer months in the Rhine River beneath the Rhine Fall, a waterfall near Schaffhausen, Switzerland. This phenomenon has been a matter of public concern ever since its first appearance, but all previous attempts to clarify the origin of this foam had remained inconclusive. With the aid of electrospray LC–MS, triterpene saponins and mono- and digalactosyldiacylglycerolipids (MGDAG and DGDAG), two classes of tensioactive metabolites occurring in the aquatic plant *Ranunculus fluitans* Lamk. (Ranunculaceae), were detected in river water and foam samples. Saponin concentrations in water and foam samples were monitored at regular intervals during the years 1998 and 2000. Other compound classes with surfactant properties such as proteins, humic acids, and synthetic detergents were also analyzed. Foam occurrence paralleled with saponin concentration and with the amounts of detached *Ranunculus* biomass accumulating at the dam of the hydroelectric power plant of Schaffhausen located just above the Rhine Fall but not with the concentration of synthetic detergents. The ecotoxicological potential of *Ranunculus* constituents, water, and foam samples was checked with a representative range of aquatic indicator organisms. No acute toxicity was observed at concentrations that were at least 50-fold higher than those found in the environmental samples.

Tiete River

Results

Santiago River (Mexico). *"Pueblos Veneno: el peligro que no se ve"*, por José Galindo, publicado en diario digital 30 minutos.

El Río Santiago se enfurece. Las espumas alcanzan los 20 metros de altura. Los que caminan por el puente que une a ambos poblados lo hacen corriendo. Los que atraviesan con auto suben sus cristales. Hay montañas de burbujas. Las espumas se desprenden del río. Tienen tamaño de almohada y vuelan en el aire. Kilómetros de río se han pintado de blanco. " La gente ahora pasa por el río y cuida que no le caiga la espuma. Pasa con sombrilla pero no para que no te caiga brisa sino para que no te vaya a caer la espuma. Si te cae en la piel te daña, es una cosa dramática",

Such a foaming phenomena have been associated to:

Uncontrolled/untreated industrial and domestic sewage are behind the pollution problem

Tiete River

Results

- 1-5 ppm of MBAS and agitation are not enough to produce such a foaming. Examples: Domestic WWTP (see below Estepona STP, Andalusia, Spain)

Tiete River

Results

Finalmente, es necesario recordar que el mismo CETESB en su informe de título "*Exportação de Poluentes do Rio Tieté através da Espuma*", con fecha Marzo de 1995, hace referencia en su página 8, al estudio de Castro & Macedo en donde ***se concluye que los tensoactivos encontrados en el Tieté son biodegradables y que la forma de resolver el problema de forma definitiva no es otra que tratar los efluentes de la ciudad de São Paulo.***

Reflexiones y Recomendaciones

Caracterización completa de vertidos (urbanos, industriales, ganaderia, etc.,)

Teniendo en cuenta sólo la contribución urbana, suponiendo un 70% de vertidos domésticos tratados, los "esgotos" de 4-5 millones de personas carecen de tratamiento

El Rio Tieté requiere un plan de saneamiento integral

Conclusions

- Las concentraciones de MBAS detectadas no son excesivamente altas, encontrándose en el rango habitual de vertidos no tratados. El porcentaje de MBAS respecto al total de materia orgánica es muy bajo.
- La revisión de la literatura científica no refleja ningún caso de espumas semejantes al del Tieté a su paso por Pirapora que puedan ser atribuidos a la presencia de tensoactivos biodegradables.
- La formación de espumas no es un fenómeno exclusivamente atribuible a los tensoactivos de origen antropogénico
- En otros ríos altamente contaminados, con problemas de espuma comparables en magnitud, se ha determinado que el origen del problema no son los detergentes.

Conclusions

- El rio Tieté ha sido y continua siendo un sumidero de vertidos de la ciudad de São Paulo, una de las mayores urbes del mundo. El río no tiene oxígeno y no reúne las condiciones para albergar vida. El rio carece de capacidad de autoregeneración.
- Achacar a los detergentes el problema de las espumas carece de rigor científico. El LAS, y el resto de tensoactivos presentes en detergentes, son perfectamente compatibles con el medio ambiente. Esta aseveración está avalada por evidencias y datos científicos. El LAS fue introducido precisamente hace 40 años para solucionar problemas de formación de espumas que no han vuelto a darse
- El problema radica en la falta de depuración de los vertidos (domésticos e industriales) de la gran urbe paulista

Obrigado pela sua atenção